

A SIMPLE PROCEDURE FOR RECOVERY OF SILVER FROM SILVER CHLORIDE USING THIOUREA

ALCÍDIO ABRÃO, ELÂINE A. JARDIM MARTINS

Instituto de Pesquisas Energéticas e Nucleares, Cx.Postal 11049-CEP 05422-970-Pinheiros, São Paulo - SP - Brasil

SYNOPSIS. – Abrão, A. & Jardim Martins, E.A. 1999. A simple procedure for recovery of silver from silver chloride using thiourea. *An. Assoc. Bras. Quím.*, 48(1), 43-45.

ABSTRACT

The use of silver in college laboratories, research institutions and at organic industry starts as silver nitrate and finishes as insoluble silver chloride. Some industrial and university laboratories maintain considerable amount of silver chloride originated from Mohr's titration of chloride with silver nitrate or titration of silver with chloride anion. Another source of silver chloride results as recycled laboratory residues or from precipitation of the solutions made by dissolving silver-bearing scraps, silver plated electronic connectors and even silverware. So, large quantities of silver chloride residues are accumulated.

This work discusses a simple and convenient method for the reclamation of silver starting from silver chloride as raw material and using thiourea both as solubilization reagent and as sulfide generation *in situ* for silver sulfide precipitation. Silver chloride is dissolved by thiourea in acidic media. The solubilization procedure can be done using sulfuric, nitric, perchloric and even hydrochloric acids. AgCl is completely dissolved at room temperature. The next step is silver sulfide precipitation simply by raising the pH of the solution. There is no hydrogen sulfide smell during the dissolution of AgCl with thiourea and its precipitation as silver sulfide. Dried silver sulfide is then calcinated to elemental silver.

The proposed method is simple, fast, safe and gives complete recovery of AgCl as metallic silver using only a few common reagents: one acid, sodium hydroxide and thiourea.

Keywords: Silver, Silver chloride and silver sulfide, Thiourea, Reclamation.

(Recebido em 15/10/98. Aceito para publicação em 15/01/99)

INTRODUCTION

Silver chloride as one of the most insoluble precipitate of silver has been mentioned in a significant number of published papers concerning problems and studies of silver. Indeed silver chloride has a paramount importance. It has been used in qualitative analysis for test and identification of silver and chloride ions and it is also valuable for the quantitative determination of both elements. The importance of silver chloride in photographic process and in electronics in general has been intensively stressed in many publications.

Actually the use of silver in college laboratories or research institutions and even at organic industry starts as silver nitrate and finishes as insoluble silver chloride. Some industrial and university laboratories maintain considerable amount of silver chloride produced from Mohr's titration of chloride with silver nitrate or titration of silver with chloride anion. Silver chloride also can come from either recycled laboratory residues or can be precipitated from solutions made by dissolving silver-bearing scraps, silver plated electronic connectors and

even silverware [1]. So, large quantities of silver chloride residues are accumulated. The use of silver nitrate often ends up as waste AgCl. It is then desirable to recycle this valuable material back again to silver nitrate directly or through elemental silver which is further dissolved with nitric acid. Silver nitrate can be used again for analytical purposes or in experiments in general and in organic chemistry [2].

In this work it is assumed that all silver residues consist entirely of AgCl.

Many procedures are published for the generation of silver nitrate from silver chloride residues and for silver reclamation.

A number of procedures for recovering silver from silver chloride have been reported. The majority of these methods usually suffer from serious drawbacks, specially using hazardous materials as cyanides or silver complexed by ammonia solution [3,4] or use quite expensive chemicals, as it is the case of the reduction of silver chloride to elemental silver by pure granular zinc in dilute sulfuric acid [5]. Sometimes, using aged dried silver chloride, its reduction by zinc/sulfuric acid is not complete [6]. It is recommended to store wet AgCl

precipitate for future reduction work, since wet silver chloride dissolves into ammonia much better than the dry material [1]. Metallic silver is obtained from silver diamine chloride solution by reduction with ascorbic acid. This procedure requires the use of excess sulfuric acid and there is gas (hydrogen) evolution, whose hazard must be considered. Reduction of the diamine silver complex is achieved also using NaBH_4 .

Some procedures use directly silver chloride for its reduction to metallic silver, as for instance reduction with aqueous sodium borohydride [6]. With sodium borohydride a vigorous reaction takes place with hydrogen evolution. Solid AgCl can be reduced with zinc or aluminum powder in acid media as well. Zinc powder has been used for reduction of AgCl to metallic silver in basic medium (NaOH). Even metallic copper powder has been used for this purpose; the excess of copper must be dissolved with aqueous ammonia and treated for final disposal. In these cases dried AgCl should be mechanically ground. Solid AgCl can be directly reduced using formaldehyde, benzaldehyde and dextrose in alkaline medium (NaOH). The electrodeposition of silver from cyanide solution is well known and widespread. This procedure is not recommended for instructional projects [7]. Oliveira, Uchimi and Bezerra published an excellent monography concerning the recover of silver from laboratory wastes [8].

Solubilization of silver chloride

Many procedures for the recovery of silver from silver chloride require this sparingly soluble salt to be dissolved. Usually this is accomplished using sodium cyanide or ammonium hydroxide. Although sodium thiosulfate could be used for the dissolution of silver chloride it has not been applied for the purpose of obtaining silver metal. The first is poisonous and the second presents explosion hazard when solutions containing the complex $[\text{Ag}(\text{NH}_3)_2]^+$ are dried. Several papers are published using these two processes to obtain metallic silver [9].

A convenient AgCl solubilization procedure

In this work a study of the action of thiourea (tu) on silver chloride was undertaken to avoid the use of the very poisonous KCN solution or the complexing with ammonia resulting in the hazardous $[\text{Ag}(\text{NH}_3)_2]^+$ when dry. The authors findings allowed to conclude that thiourea is an excellent dissolution reagent for silver chloride in acidic medium. It dissolves completely AgCl at room temperature in a slightly acidic medium, using sulfuric, nitric, perchloric and even hydrochloric acids. Absolutely there is no H_2S smell. Thiourea can be used in solution or even added as solid; in both cases the reagent is very stable and can be kept for a long time. This method is fast, safe and

gives complete dissolution of AgCl at room temperature, the resulting solution being completely clear.

Sulfide chemistry

Once the dissolution of the silver chloride with thiourea in acidic medium was achieved, the next step was to explore the thiourea ability to generate H_2S "in situ" for precipitation of silver sulfide. This was easily accomplished by neutralizing the solution containing silver and thiourea with sodium hydroxide and adding a small excess. Black silver sulfide immediately results, even at room temperature. The precipitate is coarse and dense, settling very easily and is easily filterable. In hot solutions ($50\text{--}80^\circ\text{C}$), the precipitate is denser. Again, there is no H_2S smell.

Traditional precipitation of sulfides in qualitative and quantitative analysis is made using hydrogen sulfide or ammonium hydrosulfide solutions. Triethylamine hydrosulfide has been proposed for the same purpose. To avoid the inconvenience of the disagreeable smell of the above mentioned reagents latter on it was proposed their replacement by thioacetamide. Depending on the conditions applied for the precipitation of sulfides by hydrolysis of thioacetamide some complications have been observed, for instance unexpected color of the precipitates and the formation of colloidal material, as it is the case of precipitation of mercury(II) with thioacetamide [10].

Bauer and Wehling [11] proposed the use of thiourea for the sulfide precipitation of some heavy elements, like silver, bismuth, cadmium, copper, mercury and lead. The hydrolysis of thiourea and the precipitation of metallic sulfides can be represented by the reaction: $\text{Me}^{2+} + (\text{NH}_2)_2\text{CS} \rightarrow \text{MeS} + \text{NH}_4\text{CN} + 2\text{H}^+$.

Thiourea is sometimes used as a complexing agent for copper and other metallic cations, for instance to prevent their interference in colorimetric methods, or used to strip some metal from an organic phase or even avoid their extraction to an organic solvent phase [12]. Copper(II) ion is reduced and the colorless complex $[\text{Cu}(\text{tu})]^+$ is formed. Complexes interesting to be mentioned are $[\text{Bi}(\text{tu})_6]^{3+}$, $[\text{Cd}(\text{tu})_3]^{2+}$, $[\text{Hg}(\text{tu})_4]^{2+}$, $[\text{Pb}(\text{tu})_3]^{2+}$ and $[\text{Ag}(\text{tu})_3]^+$. These complexes are relatively stable in acidic solution at room temperature, but on neutralization and alkalization of the solutions the correspondent sulfides are precipitated. This is the case of silver, reported in the present paper. In this case we stress its use with the convenience of not producing any unpleasant smell, it is an inexpensive reagent, easily supplied by reagent houses and has no risk or hazards, as it is the case of thioacetamide, heavily suspected as a carcinogen reagent [13]. Especially for undergraduate courses, students can use thiourea without any risk or danger, unlike the cases of hydrogen sulfide, ammonium hydrosulfide and thioacetamide.

Conversion of silver sulfide to silver metal

Once prepared the silver sulfide precipitate is washed, dried and then calcinated to the metal: $\text{Ag}_2\text{S}(\text{s}) + \text{O}_2 \rightarrow 2\text{Ag}(\text{s}) + \text{SO}_2$. Using an alumina crucible the sulfide is calcinated in an air atmosphere into a furnace or even using a Bunsen burner. A small aliquot of the obtained silver can be laminated with the aid of a spatula using a glass or porcelain plate and its metallic shine can be easily observed by the student.

DISCUSSION

Thiourea forms complexes of the amine type with several heavy metals, most of which are colorless (e.g. silver, mercury, thallium). The stability constant of the silver complex with thiourea $[\text{Ag}(\text{tu})_3]^+$ is $K = 7.10 \cdot 10^{-14}$ (pK 13,14). Its correspondent complex with ammonia $[\text{Ag}(\text{NH}_3)_2]^+$ has a constant $K = 9.31 \cdot 10^{-8}$ (pK 7,03). Chief among the elements giving colored products in acid solution are bismuth (yellow), tellurium (yellow), osmium (red) and ruthenium (blue).

Thiourea is stable in solution at room temperature but decomposes slowly at higher temperatures. One of the hydrolysis products is hydrogen sulfide.

It is worth knowing the difference in the solubilization of silver chloride using ammonia, sodium thiosulfate or sodium cyanide in alkaline media and its dissolution by the proposed procedure, with thiourea in slightly acidic medium. The safety aspect can be emphasized. Of high significance in inorganic and analytical chemistry is complex formation of metallic ions with several ligands. It is interesting to stress the complexing action of ammonia, cyanide and thiourea with the silver cation. The dissolution of AgCl by complex ion formation is demonstrated.

The next chemical reaction is precipitation of the silver sulfide, using the same reagent, that is, thiourea, already introduced for the formation of the soluble $[\text{Ag}(\text{tu})]^+$ complex and solubilization of silver chloride. Silver sulfide precipitation is done easily by simply adding sufficient sodium hydroxide to hydrolyze the silver complex to sulfide. This operation is done even at room temperature. It is observed a total absence of unpleasant hydrogen sulfide smell. Let's remember here that silver sulfide is a very insoluble salt, with a SP of $3.3 \cdot 10^{-52} \text{ mol}^2\text{L}^{-2}$.

The precipitate is black, coarse, dense, easily filtered. After washed with water and dried it is calcinated to metallic silver.

The reader is invited to discuss the utility and importance of the pyrometallurgical process involving some sulfides in the industry, as in the cases of copper sulfide, iron sulfide, lead sulfide, that can be calcinated in air (oxygen) for transformation of the

corresponding oxides to metals (CuS and Cu_2S to Cu , FeS to FeO , PbS to PbO and Ag_2S to Ag).

A Simplified Procedure

The silver chloride residue, aged or recently precipitated from silver solution with sodium chloride or hydrochloric acid is filtered and washed first with water several times and then with dilute nitric acid to remove some contaminants like copper, nickel, cobalt, iron, zinc and lead ions, and finally washed again with water.

Transfer the precipitate to a beaker using water, cover the precipitate with dilute acid solution (nitric, sulfuric and even hydrochloric acid) and then add dropwise the thiourea solution (aqueous 100 g.L^{-1} solution) or thiourea crystals, agitating manually (mechanical stirrer can be used) until the precipitate is dissolved.

Add a dilute sodium hydroxide solution until the solution becomes slightly alkaline. Immediately black silver sulfide is precipitated. After a few minutes filter the precipitate and wash with water, dry in an oven (80 to 110°C) and finally calcinate the silver sulfide in an alumina crucible. After cooling, metallic silver is removed.

REFERENCES

- Hill, James W. & Lena Bellows. 1986. *J.Chem.Educ.*, 63, 357.
- Garin, D.L. & Henderson, K.O. 1970. *J.Chem.Educ.*, 47, 741.
- Bush, J.B. & Diehl, H.J. 1979. *J.Chem.Educ.*, 56, 84.
- Thall, E. 1981. *J.Chem.Educ.*, 58, 561.
- Foust, D.F. 1984. *J.Chem.Educ.*, 61, 925.
- Murphy, J.A., Ackerman, A.H. & Heeren, J.K. 1991. *J.Chem.Educ.*, 68, 603.
- Johnson, K. & Harvey, D. 1979. *J.Chem.Educ.*, 56, 54.
- Oliveira, D.; Uchimi, F.Y. & Bezerra, S.R. 1983. Métodos de recuperação e reciclagem de prata de rejeitos de laboratório; Coordenação: Miuaco K.Kuya, Instituto de Química, Universidade de São Paulo.
- Perman, C.A. 1979. *Talanta*, 26, 603.
- Vozza, J.F. 1958. *J.Chem.Educ.*, 35, 145.
- Bauer, R. & Wehling, I. 1964. *Z.anal.Chem.*, 199, 171.
- Abrão, A. 1976. Technology of uranium purification. Impurities decontamination from uranyl chloride by extraction with tri-n-octylamine in the presence of thiourea as complexing ligand. Publ.IEA-458, Instituto de Energia Atomica, São Paulo.
- Kevin, R. 1993. *J.Chem.Educ.*, 70, 855.